

Y-2052

**DURABILITY OF ADHESIVE BONDS TO
URANIUM ALLOYS, TUNGSTEN,
TANTALUM, AND THORIUM**

F. G. Childress

June 1976

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**DURABILITY OF ADHESIVE BONDS TO URANIUM ALLOYS,
TUNGSTEN, TANTALUM, AND THORIUM**

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ABSTRACT

Long-term durability of epoxy bonds to alloys of uranium, nickel-plated uranium, thorium, tungsten, tantalum, tantalum-10% tungsten, and aluminum has been evaluated. Significant strengths remain after ten years of aging; however, there is some evidence of bond deterioration with uranium alloys and thorium stored in ambient laboratory air.

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SUMMARY

Adhesive-bonding studies have been performed and tests made after ten years of aging to bonds of aluminum, tungsten, thorium, tantalum, and uranium alloys. A considerable number of chemical etchants and combinations were evaluated prior to initiation of the aging study. The adhesives were selected somewhat arbitrarily on the basis of past experience.

The results of the aging study indicate that:

1. Epoxy-bonded specimens of uranium alloys, tungsten, thorium, tantalum, and aluminum retain significant strength after aging in air for ten years.
2. Adhesive bonds to corrosion-resistant uranium alloys and thorium deteriorate slowly in ambient laboratory air, but retain full integrity in dry nitrogen.

INTRODUCTION

An adhesive aging study was initiated with three corrosion-resistant alloys of uranium [U-6.5% Nb; U-8.5% Nb; and U-7.5% Nb-2.5% Zr (Mulberry)] nickel-plated uranium, thorium, tungsten, tantalum, and tantalum-10% tungsten. Surface-preparation techniques were evaluated and established for these tests for each alloy. Epoxy formulations were selected for all aging studies.

The purpose of this study was to determine if these metals and alloys would withstand long-term storage in air with no impairment. This work was performed at the Oak Ridge Y-12 Plant.^(a)

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

DURABILITY OF ADHESIVE BONDS

SURFACE TREATMENT AND ADHESIVE SELECTION

A number of preliminary evaluations were made to determine and to adopt a specific procedure for the surface preparation of each metal and alloy. Very little information of this type was available. Standardization was necessary to obtain meaningful data from the aging studies.

Selection of suitable surface treatments for chemically etching or cleaning the uranium alloys and thorium proved to be difficult. The treatments selected were not necessarily the optimum as they were not evaluated on the basis of bond strength. Many variations of acids, concentrations, and blends were tried, along with caustic solutions. All treatments that were effective in etching or discoloring the alloys were also variable in their behavior, lending some doubt as to their reproducibility with large parts. The selected treatments were chosen principally by visual appearance of the surfaces that were obtained from arbitrarily selected time-of-immersion tests on butt ends of the specimens to be used. Freshly machined surfaces were used for each test as it did not appear that multiple immersions created the same effect as one, continuous, equal-time immersion. Surfaces treated in basically the same manner were often quite different in appearance. These differences may have resulted from: (1) differences in the base alloy, (2) slight differences in the bath temperature, (3) differences in the amount of bath agitation, (4) possible catalytic effect of the dissolution of the alloy, and (5) the time lapse between etching and rinsing.

Other factors that entered into the selection criteria were: (1) degree of discoloration, (2) oxidation resistance under ambient conditions, (3) water-break characteristics, and (4) reproducibility. The solutions and etch procedures used in all the long-term tests are listed in Table 1.

To determine the relative effectiveness of the chemical-etch treatments, a number of specimens were assembled with no surface preparation other than solvent degreasing. Similar specimens for comparison were sandblasted, degreased, and assembled for all metals and alloys except the uranium binary alloys and thorium. Strengths of the sandblasted specimens, as reported in Table 2, are approximately twice that of the solvent-cleaned specimens and approximately the same as the strengths of the chemically etched specimens.

Adhesive systems selected for all aging tests were composed of the standard epoxy resin [diglycidyl ether of bisphenol A (Epi-Rez-5101(b) or Epon 828(c))], polyamide resins (Versamid(d) 125 or 140), and an amine adduct (Curing Agent U(c)). The specific formulations (Systems 1 and 4 in Table 3) are essentially the same. These systems perhaps offer nothing unique over a variety of amine-cured systems as far as aging stability is concerned. They consist almost entirely of carbon, hydrogen, oxygen, and nitrogen, with

(b) A Celanese product.

(c) A Shell product.

(d) A General Mills product.

Table 1
ETCH SOLUTIONS AND PROCEDURES

| Metal | Etch Composition and Weight Ratio ⁽¹⁾ | Procedure ⁽²⁾ |
|--------------------------------|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| Aluminum | H ₂ O(30) : H ₂ SO ₄ (10) : Na ₂ Cr ₂ O ₇ (1) | Etched for 15 minutes at 165° F; rinsed. |
| Mulberry (U-7.5 Nb-2.5 Zr) | H ₂ O(400) : HCl(100) : HF(0.5) | Immersed for 30 seconds, rinsed; immersed for 15 seconds, rinsed; immersed for 10 seconds, rinsed. |
| Binary Alloys (U-Nb) | H ₂ O(50) : HNO ₃ (25) : HF(25) | Etched for one minute, rinsed. |
| | H ₂ O(80) : HNO ₃ (20) | Immersed for 15 minutes, rinsed. |
| | H ₂ SO ₄ (10) : H ₃ PO ₄ (90) | Electrocleaned at 10 volts for 30 seconds, rinsed. |
| Tantalum and Tantalum-Tungsten | H ₂ O(50) : HNO ₃ (25) : HF(25) | Etched for 30 minutes, rinsed. |
| Tungsten | H ₂ O(50) : HNO ₃ (25) : HF(25) | Etched for one minute, rinsed. |
| Thorium | H ₂ O(35): Amchem Deoxidizer 1 (1) : HNO ₃ (12) | Etched for 15 minutes, rinsed. |

(1) Weight ratio was on the basis of commercial reagents; viz: concentrated H₂SO₄, 95 - 98%; HNO₃, 70 - 71%; HCl, 36.5 - 38%; HF, 48%; H₃PO₄, 85%.

(2) All treatments except that for aluminum were performed at room temperature.

Table 2
TENSILE SHEAR STRENGTH PRELIMINARY TESTS

| Specimen Type | Number of Specimens | Surface Preparation ⁽¹⁾ | Adhesive System ⁽²⁾ | Strength | |
|---------------|---------------------|------------------------------------|--------------------------------|----------|--------------------|
| | | | | MPa | Standard Deviation |
| W/Al | 5 | Solvent Cleaned | 1 | 7.2 | 1.8 |
| | 5 | Sandblasted and Solvent Cleaned | 1 | 15.1 | 1.7 |
| Ta/Al | 5 | Solvent Cleaned | 1 | 5.9 | 1.1 |
| | 5 | Sandblasted and Solvent Cleaned | 1 | 12.5 | 3.2 |
| Ta-10W/Al | 4 | Solvent Cleaned | 1 | 10.8 | 2.0 |
| | 5 | Sandblasted and Solvent Cleaned | 1 | 15.0 | 2.8 |
| Mulberry/Al | 5 | Solvent Cleaned | 1 | 7.7 | 1.9 |
| | 4 | Sandblasted | 1 | 12.3 | 2.2 |
| | 6 | Sandblasted | 2 | 9.2 | 2.3 |
| | 6 | Etched | 2 | 10.6 | 2.1 |
| | 5 | MEK ⁽³⁾ Wiped | 3 | 6.0 | 1.4 |
| | 5 | Etched | 3 | 13.1 | 3.0 |

(1) Solvent cleaned: methylene chloride dip followed by methyl ethyl ketone (MEK) dip. All aluminum surfaces were etched. Table 1 lists all etch solutions and procedures.

(2) See Table 3. All systems were cured at room temperature as follows: System 1 - 3 weeks, System 2 - 1 week, System 3 - 2 weeks.

(3) Methyl ethyl ketone.

very little impurities. The preliminary tests (reported in Table 2) also used two other adhesives with Mulberry. All aging tests were made with Adhesive 1 (see Table 3) except with thorium in which case Adhesive 4 was used.

SPECIMEN PREPARATION

Adhesive specimens were fabricated, per ASTM Procedure D-1002, from all the metals and alloys previously listed. These specimen components were 100 mm long, 25 mm wide, and 1.6 mm thick. A mixed total of 481 tensile shear specimens were bonded with the selected adhesives. One

adherend of each specimen was aluminum (alloy 2024-T-3), selected because of its low cost and because it was believed that desirable information could be obtained by comparing the failures at the adhesive-to-aluminum interface with failures at the adhesive-to-test metal interface.

Sufficient specimens of each type were bonded to provide at least four randomized groups of five specimens each. At least twice this number of groups of the uranium alloys and thorium were bonded to permit aging under both ambient-air and dry-nitrogen atmospheres. Extra groups of Mulberry specimens were provided to permit additional aging tests. In this case, eleven specimens were used in each group. The number of specimens used in some cases was limited by their availability.

Randomized groups of each specimen type were prepared and set aside to age under either ambient-laboratory-air or dry-nitrogen atmospheres. Each of these groups except the Mulberry control group had near-equal representation from each bonding group population, making the groups statistically related to each other.

RESULTS

Based on strength data, as reported in Tables 4 through 6, no statistically significant changes are apparent as a function of the aging time. However, without exception, every group aged under dry nitrogen had a greater average strength than its comparative group aged in ambient laboratory air. Since there were no significant differences, all uranium alloy groups were averaged. Overall strength of specimens stored in dry nitrogen was 12.6 MPa, compared to 10.6 MPa for those stored in ambient laboratory air. Respective averages of thorium specimens was 14.2 versus 12.3 MPa, whereas the nickel-plated uranium averaged 6.4 and 5.0 MPa, respectively. The overall averages of the tantalum and tungsten groups ranged from 13 to 14 MPa.

A higher percentage of adhesive failure occurred on the alloy surface of all air-aged groups than on the comparable nitrogen-aged groups. Visual evaluation of the failed specimens

Table 3
ADHESIVE SYSTEMS

| System | Component | Weight Ratio |
|--------|----------------|--------------|
| 1 | Epi Rez 5101 | 100 |
| | Versamid 125 | 25 |
| | Curing Agent U | 10 |
| 2 | Epi Rez 5101 | 100 |
| | Versamid 140 | 60 |
| 3 | Epon 934 A | 100 |
| | Epon 934 B | 33 |
| 4 | Epon 828 | 100 |
| | Versamid 140 | 25 |
| | Curing Agent U | 10 |

Table 4
AGING DATA OF THE URANIUM ALLOY BONDS TO ALUMINUM

| Time Aged, t(1) | Aging Atmosphere(2) | Test Data(3) | | | | | | | | | | | |
|-----------------------|------------------------|--------------|----------|---|----|-------------|----------|---|----|--------------------|----------|----|----|
| | | U-6.5 Nb/Al | | | | U-8.5 Nb/Al | | | | U-7.5 Nb-2.5 Zr/Al | | | |
| | | MPa | σ | n | % | MPa | σ | n | % | MPa | σ | n | % |
| 1 Month | Ambient | 13.5 | 3.6 | 6 | 62 | 10.3 | 1.3 | 5 | 43 | 12.6 | 1.7 | 10 | 80 |
| 1 Year | Ambient | 10.5 | 1.2 | 6 | 82 | 10.5 | 1.6 | 4 | 26 | 10.1 | 1.1 | 11 | 90 |
| | N ₂ | 12.1 | 2.2 | 6 | 35 | 12.1 | 2.1 | 5 | 22 | 11.3 | 1.7 | 11 | 78 |
| 2 Years | Ambient | 9.9 | 1.9 | 6 | 91 | 8.8 | 1.5 | 5 | 95 | 10.6 | 1.7 | 11 | 99 |
| | N ₂ | 13.4 | 1.1 | 6 | 38 | 11.0 | 2.3 | 5 | 30 | 11.4 | 1.4 | 11 | 75 |
| 3 Years | Ambient | | | | | | | | | 11.1 | 1.4 | 11 | 97 |
| | N ₂ | | | | | | | | | 11.8 | 1.6 | 11 | 88 |
| 5 Years | Ambient | 8.9 | 1.9 | 6 | 97 | 10.6 | 1.6 | 5 | 82 | 9.4 | 2.3 | 11 | 94 |
| | N ₂ | 13.7 | 3.2 | 5 | 58 | 14.3 | 1.4 | 5 | 72 | 13.4 | 2.1 | 11 | 57 |
| 10 Years | Ambient | 11.3 | 0.9 | 5 | 85 | 11.4 | 0.9 | 3 | 92 | 10.3 | 1.3 | 11 | 99 |
| | N ₂ | 13.0 | 1.3 | 5 | 45 | | | | | 13.4 | 1.6 | 11 | 74 |

(1) All specimens were cured and aged at room temperature.

(2) Ambient laboratory air; dry nitrogen.

(3) MPa, average tensile shear strength; σ , standard deviation; n, number of specimens; %, percent adhesive failure on the nonaluminum surface.

Table 5
AGING DATA FOR THE ADHESIVE BONDS OF TUNGSTEN, TANTALUM,
AND TANTALUM-10 TUNGSTEN TO ALUMINUM

| Time Aged, t(1) | Test Data(2) | | | | | | | | | | | |
|-----------------------|--------------|----------|---|----|-------|----------|---|----|-----------|----------|---|----|
| | W/Al | | | | Ta/Al | | | | Ta-10W/Al | | | |
| | MPa | σ | n | % | MPa | σ | n | % | MPa | σ | n | % |
| 1 Month | 13.6 | 1.4 | 6 | 52 | 13.7 | 2.9 | 6 | 50 | 11.7 | 2.0 | 5 | 76 |
| 1 Year | 14.1 | 1.0 | 6 | 55 | 14.7 | 2.1 | 6 | 83 | 13.2 | 2.0 | 5 | 48 |
| 2 Years | 13.9 | 3.3 | 6 | 50 | 13.2 | 2.8 | 6 | 74 | 13.9 | 2.9 | 5 | 75 |
| 5 Years | 13.4 | 4.3 | 6 | 59 | 11.6 | 3.9 | 6 | 92 | 12.3 | 3.2 | 5 | 98 |
| 10 Years | 15.0 | 3.6 | 6 | 62 | 11.6 | 3.6 | 6 | 88 | 14.6 | 2.9 | 5 | 90 |

(1) All specimens were cured at room temperature and aged in ambient laboratory air.

(2) MPa, average tensile shear strength; σ , standard deviation; n, number of specimens; %, percent adhesive failure on the nonaluminum surface.

indicates more conclusively than the test data that aging in air is detrimental to bond integrity. All aged-in-air uranium alloy specimens, when failed, revealed a band of oxidation around the perimeter of the bonded area, as indicated on the left side of Figure 1. This "picture-frame" effect is not observable on the nitrogen-aged specimens (right side). The top two specimens on both sides of the photograph are the two binary alloys; the bottom two specimens are Mulberry.

Table 6
AGING DATA FOR ADHESIVE BONDS OF THORIUM AND
NICKEL-PLATED URANIUM TO ALUMINUM

| Time Aged, t(1) | Aging Atmosphere | Test Data(2) | | | | | |
|-----------------------|---------------------|--------------|----------|----|----------------|----------|----|
| | | Th/Al | | | Ni-Plated U/Al | | |
| | | MPa | σ | n | MPa | σ | n |
| 1 Day | Ambient | 15.1 | 1.6 | 12 | | | |
| 2 Weeks | Ambient | | | | 6.5 | 1.0 | 10 |
| 5 Months | Ambient | 12.6 | 1.0 | 4 | | | |
| | N ₂ | 14.1 | 1.9 | 4 | | | |
| 12 Months | Ambient | | | | 5.4 | 1.2 | 6 |
| | N ₂ | | | | 6.2 | 1.5 | 6 |
| 15 Months | Ambient | 13.5 | 1.8 | 4 | | | |
| | N ₂ | 14.5 | 2.1 | 4 | | | |
| 2 Years | Ambient | 11.0 | 1.6 | 4 | | | |
| | N ₂ | 13.5 | 0.6 | 4 | | | |
| 3 Years | Ambient | | | | 4.7 | 0.7 | 6 |
| | N ₂ | | | | 6.1 | 1.8 | 6 |
| 9 Years | Ambient | 12.1 | 1.2 | 4 | | | |
| | N ₂ | 14.6 | 1.8 | 4 | | | |
| 10 Years | Ambient | | | | 3.6 | 1.6 | 8 |
| | N ₂ | | | | 5.9 | 0.7 | 6 |

(1) All specimens were aged at room temperature. Th/Al specimens aged for one day were heat cured at 74° C/16 hours; all others, room-temperature cured.

(2) MPa, average tensile shear strength; σ , standard deviation; n, number of specimens.

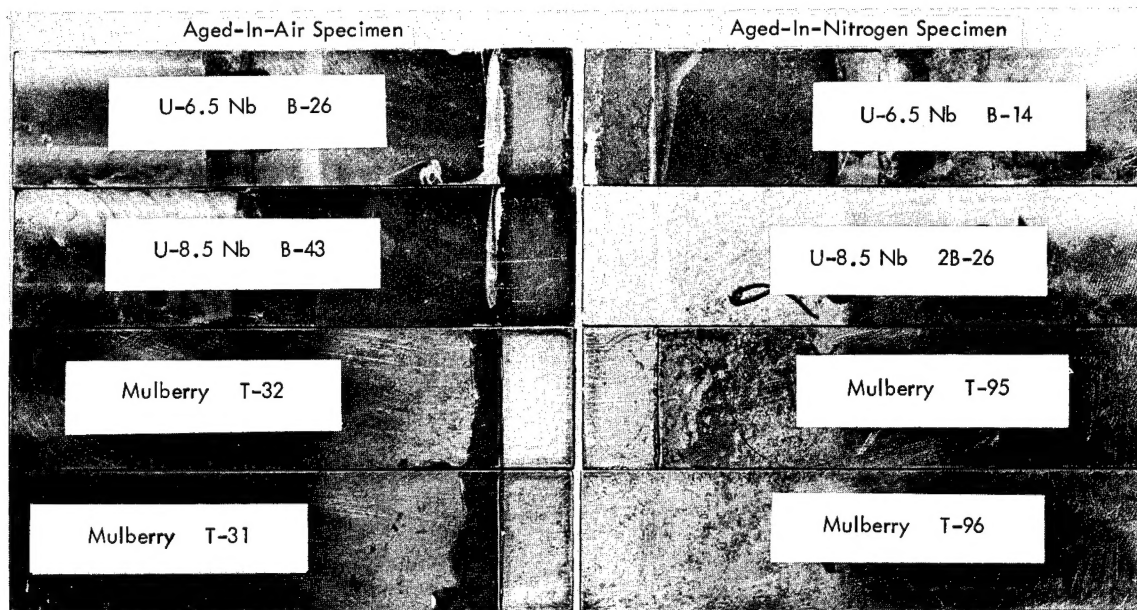


Figure 1. AGED ADHESIVE SPECIMENS.

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The picture-frame effect is not observable with thorium. Specimens aged nine years in air, however, appear to have darkened considerably in comparison to those aged in dry nitrogen. Darkening occurred under the adhesive as well as in the exposed areas. The nine-year, ambient-aged specimens failed cleanly on the thorium surfaces, whereas the dry-nitrogen-aged specimens failed evenly on the thorium and aluminum surfaces. The latter specimens had no tarnished appearance.

Aging data indicate no significant change in the strength of the bonded specimens of tungsten, tantalum, and tantalum-10% tungsten after ten years in air (ambient laboratory conditions). Table 5 reports these results.

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